3μm - 1.6μm DOUBLE RESONANCE SPECTROSCOPY OF CH_4

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The Near-IR Spectrum of CH_4 is dense with many overlapping bands that perturb each other by vibrational and ro-vibrational interactions. Assignments of the individual lines are needed in order to simulate the spectrum as a function of pressure and temperature, as needed in the search for CH_4 in extrasolar planets. Both the group at the University College, London[1] and that at the University of Reins[2] have produced theoretical spectra that allows simulation up to the high temperatures expected on "Hot Jupiters". The accuracy of these theoretical spectra need to be further tested.

Because CH_4 is a light spherical top, assignment of its perturbed spectra is a formable challenge as none of the lines allowed in the rigid rotor approximation have ground vibrational state combination differences. We are using IR-IR double resonance to observe modulation in the strength of near-IR absorption caused by a modulation of a 3 μm OPO beam that is tuned to a particular transition in the C-H stretching fundamental of CH_4. This produces V-type double resonance transitions (which share the lower state with the pump transition), which provides firm assignments for lines normally observed in absorption in the near-IR. We also observe sequential double resonance which reveals transitions that have a known rotational level of the ν_3 fundamental as the lower state and reaches final states in the 9000 cm^{-1} spectral region. These are states of *A, E,* F_1 vibrational symmetries which are forbidden in transitions from the ground vibrational state. These 3 level double resonance transitions are Doppler Free and have a linewidth of $\sim$10 MHz due to a combination of near-IR laser jitter and power broadening of the mid-IR transition. We also observed many 4-level double resonance transitions that we have tentatively assigned as arising from the ν_4 fundamental level. These are distinguished from the 3-level double resonance transitions by they being Doppler broadened and having a large phase shift relative to the intensity modulation.

1. S.N. Yurchenko, PNAS **111** 9379-83 (2014); 2. M. Rey, JQSRT **18**, 207-220 (2015), PCCP **18**, 176-189 (2016)